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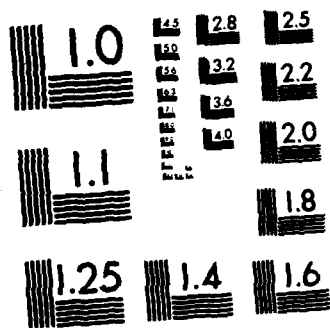
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Metal Substituted Cumylphenoxy Phthalocyanines
for use as Gas Sensing Semiconducting Films

by

Neldon L. Jarvis
Arthur W. Snow
Henry Wohltjen

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**METAL SUBSTITUTED CUMYLPHENOXY PHTHALOCYANINES
FOR USE AS GAS SENSING SEMICONDUCTING FILMS**

Nelson L. Jarvis¹
Arthur W. Snow
Henry Wohltjen

ABSTRACT

A series of cumylphenoxy phthalocyanines derivatives, including the metal free and the Cu, Co, Ni, Pd and Pt substituted, were synthesized and characterized. Each compound exhibited appreciable solubility in solvents such as benzene and toluene, and formed stable, insoluble monomolecular films when spread at the water/air interface. Film pressure vs area/molecule isotherms were determined for each derivative and the results discussed in terms of possible molecular orientations. Techniques were established to prepare Langmuir-Blodgett films of the phthalocyanine derivatives and to measure their electrical properties.

INTRODUCTION

Monolayer and multilayer films of polar organic compounds are of considerable interest for their potential applications in electronic devices. Organic films of molecular dimensions are being investigated for such properties as photoconductivity (2,3,4), insulating barriers in amorphous silicon MIS structures (5), electrical conductivity (field effect devices) (6), and ultra-thin photoresists (7,8). The Langmuir-Blodgett (L-B) technique for the formation of mono- and multilayer films is of special interest as it can produce films with known molecular orientation and composition. L-B films can also be prepared relatively free of pinholes and other defects and can be prepared to a specific thickness (number of monolayers). In addition layers of different chemical composition can be deposited in specific order (2,3) to give desired electrical or photo responses.

The many advantages of the Langmuir-Blodgett films can only be realized, however, with organic molecules that form stable, insoluble monomolecular films at the water/air interface, and that will transfer under a given film pressure to solid substrates of interest. The use of L-B films for specific electrical and electronic applications will therefore require the design, synthesis and characterization of high purity film-forming materials that will respond to a desired stimulus or chemical environment.

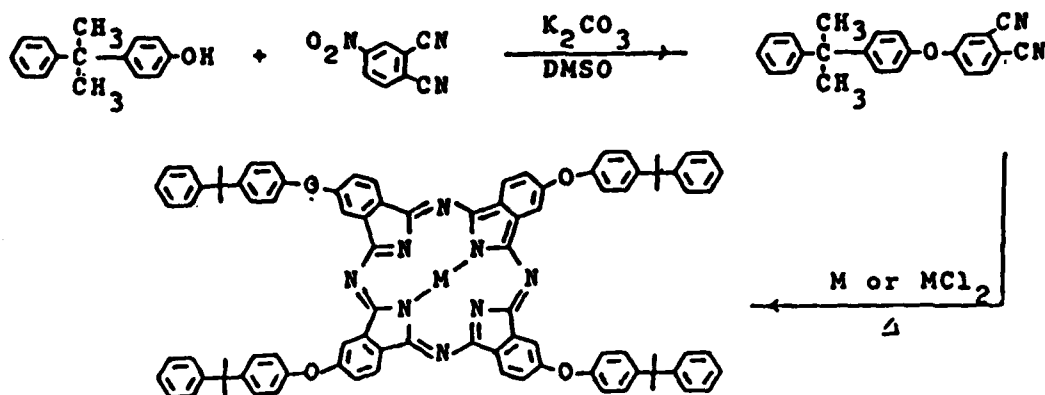
In the present study we are interested in the development of mono- and multilayer L-B films that change electrical properties upon exposure to very small concentrations of toxic gases. It is known that the electrical properties of semiconductors are greatly affected by the presence of small amounts of impurities, which suggests that organic semiconducting films could be used effectively as sensors for chemical impurities. Furthermore the use of an organic semiconductor offers an enormous array of possibilities for enhancing chemical selectivity through appropriate modification of the organic molecular composition and structure. Changes in the electrical properties of the organic semiconductors will ultimately be determined using microfabricated surface conductivity cells having a very large number of closely spaced interdigital electrodes. In this way easily measured currents can be obtained with bias voltages of one volt or less. Such low voltages should reduce any electrode reactions and alleviate many potential drift problems.

EXPERIMENTS

Synthesis and Characterization of Organic Semiconductor

The phthalocyanine macrocycle has been a structure of considerable interest since originally determined by Linstead (9). It is a powerful ligand for both transition and nontransition metals, and its family of compounds has been investigated as electrical semiconductors, photovoltaic and electrochromic materials, and as oxidation and photo-oxidation catalysts (10). With the exception of the lithium derivatives, however, the phthalocyanines themselves are very difficult to handle due to their exceedingly low solubility in organic solvents. The first objective of this research therefore was to prepare and characterize phthalocyanine derivatives with adequate solubility in a variety of organic solvents and amenable to purification by column chromatography. Metal substituted cumylphenoxy phthalocyanines were therefore selected for synthesis and study in this investigation.

The cumylphenoxy phthalocyanine synthesis is described in Scheme I. Cumylphenoxyphthalonitrile is prepared by a nitro-displacement reaction of cumylphenol and 4-nitrophthalonitrile. The metal phthalocyanines (M=Cu, Ni, Co, Pd, Pt) are generated by heating the phthalonitrile in the presence of finely dispersed metals or chloride salts. The metal-free phthalocyanine is prepared by heating the phthalonitrile in the presence of an organic nucleophilic reducing agent such as hydroquinone or tetrahydropyridine. The phthalocyanine products are characterized by visible, infrared, NMR and ESR spectroscopic and elemental analysis.



4-Cumylphenoxy-4-phthalonitrile (I). I was prepared by K_2CO_3 catalyzed nitrodisplacement of 4-nitrophthalonitrile (Eastman) by cumylphenol (Aldrich) in DMSO. In a nitrogen atmosphere, 19.56 g (0.141 mole) of finely ground anhydrous K_2CO_3 were added to a solution of 19.08 g (0.090 mole) 4-cumylphenol and 15.57 g (0.090 mole) 4-nitrophthalonitrile in 150 ml dry DMSO by 1 to 2 g additions at 1/2 to 1 hr. intervals over an 8 hour period. The mixture was stirred for 24 hours at 20°C under nitrogen. The reaction was worked up by filtering the undissolved salt and slowly adding the filtrate to a rapidly stirred 400 ml volume of water. The suspension was neutralized with HCl, and the crude product taken up into 100 ml methylene chloride and combined with two subsequent 50 ml extractions. The methylene chloride solution was then extracted with 100 ml 5% Na_2CO_3 to remove unreacted phenol, washed, dried and solvent stripped to yield 21.3 g (70%) I. The crude product was recrystallized twice from methanol yielding large platelets, MP=90°C. Analysis. Calc. for $C_{23}H_{18}N_2O$: C, 81.65; H, 5.32; N, 8.23. Found: C, 81.86; H, 5.28; N, 8.23. On standing for several weeks the platelet crystals turn light green which is associated with the presence of a trace quantity of occluded methanol. Recrystallization from hexane proceeds with difficulty but yields needle shaped crystals MP=90°C, which remain colorless indefinitely. Analysis. Found: C, 81.72; H, 5.41; N, 8.33. IR (KBr) 3080-3020 (=C-H), 2238 (CN), 1580 (C-C), 1500-1430 (aromatic); NMR ($CDCl_3$) δ 1.70 (Singlet, 6H), δ 7.27 (multiplet, 12H); mass spect. parent ion 338.

Tetracumylphenoxy metal-free phthalocyanine (II). II was prepared reacting I with hydroquinone at a 4:1 mole ratio in an evacuated sealed tube. To a 10 x 75 mm tube were added 1.00 g (2.96 m mole) I and 0.081 g (0.74 m mole) hydroquinone (purified by sublimation). The mixture was fused by gentle heating to a uniform solution and placed in a 165°C oven for 16 hrs. The crude product was purified by dissolving in toluene and passing through an alumina (grade 1) column with dioxane elution. The dioxane solution was concentrated to a 5 ml volume and the phthalocyanine was

precipitated by dropwise addition into a stirred volume of 200 ml of methanol. The flocculant blue precipitate was filtered into the thimble of a micro soxhlet extractor, extracted with methanol to insure complete removal of unreacted phthalonitrile, and extracted into benzene. The benzene solution was concentrated to a 5 ml volume and added dropwise to a stirred volume of 200 ml petroleum ether. The flocculant blue precipitate was collected 0.49 g (49%), dried and analyzed. Analysis, calc. for $C_{22}H_{14}N_8O_4$: C, 81.51; H, 5.50; N, 8.27. Found: C, 81.61; H, 5.62; N, 8.43 (no residue observed). IR (supported film on NaCl) 3290 (N-H), 3090-3030 (=C-H), 1608 (C=C), 1510-1470 (aromatic). NMR (CD_2Cl_2) δ 1.72 (singlet 12 H), δ 7.32 (multiplet, 24 H). Visible-UV (dioxane) 697 ($\epsilon=1.41 \times 10^5$ l/cm mole), 663, 635, 602, 390, 341, 286.

Tetracumylphenoxy copper phthalocyanine (III). To a 10 x 75 mm tube with a teflon coated micro stirring bar were added 0.676 g (2.00 mmole) I and 0.245 g (4.00 mg-atom) copper bronze (Creslite). The mixture was fused at 200°C under vacuum for complete removal of residual methanol occluded in I and sealed under vacuum. The entire tube was heated at 270°C with stirring for 12 hrs. The workup procedure was identical to II and yield was 43%. Analysis. Calc. for $C_{92}H_{72}N_8O_4Cu$, 4.48; C, 78.00; H, 5.12; N, 7.91. Found: Cu, 4.61; C, 78.19; H, 5.01; N, 7.99. IR (supported film on NaCl) 3090-3030 (=C-H), 1608 (C=C), 1510-1470 (aromatic). NMR ($CDCl_3$) δ =1.65 (very broad singlet 12 H), 7.25 (broad singlet 24 H). ESR broad singlet $g = 2$. Visible-UV (dioxane) 674 ($\epsilon=2.05 \times 10^5$ l/cm mole), 606, 347, 280.

Tetracumylphenoxy nickel phthalocyanine (IV). To a 10 x 75 mm tube with a teflon coated micro stirring bar were added 0.676 g (2.00 mmole) I and 0.235 g (4.00 mg-atom) nickel powder (HCl cleaned, washed and dried). The mixture was fused under vacuum for complete removal of residual methanol occluded in I and sealed under vacuum. The entire tube was heated at 280°C with stirring for 44 hrs. Work up procedure was identical to II and the yield was 76%. Analysis. Calc. for $C_{92}H_{72}N_8O_4Ni$: Ni, 4.16; C, 78.23; H, 5.14; N, 7.93. Found: Ni, 3.96; C, 78.00; H, 5.23; N, 7.82. IR (supported film on NaCl) 3090-3030 (=C-H), 1608 (C=C), 1510-1470 (aromatic). ESR broad singlet $g = 2$. Visible-UV (dioxane) 667 ($\epsilon=1.57 \times 10^5$ l/cm mole), 600, 340, 290.

Tetracumylphenoxy palladium phthalocyanine (V). To a 10 x 75 mm tube with a teflon coated micro stirring bar were added 0.676 g (2.00 mmole) I and 0.088 g (0.50 mg-formula wt) $PdCl_2$ (Alfa). The mixture was fused at 200°C under vacuum for complete removal of residual methanol occluded in I and sealed under vacuum. The entire tube was heated at 290°C with stirring for 2 days. Workup procedure was identical to II and the yield was 15%. Analysis. Calc. for $C_{92}H_{72}N_8O_4Pd$: Pd, 7.29; C, 75.68; H, 4.97; N, 7.67. Found: Pd, 7.25; C, 75.94; H, 4.99; N, 7.35. IR (supported film on NaCl) 3090-3030 (=C-H), 1608 (C=C), 1510-1740 (aromatic). Visible-UV (dioxane) 660 ($\epsilon=1.37 \times 10^5$ l/cm mole) 612, 329, 283.

Tetracumylphenoxy platinum phthalocyanine (VI). To a 10 x 75 mm tube with a teflon coated micro stirring bar were added 1.00 g (2.96 mmole) I and 0.10 g (.376 mg-formula wt) $PtCl_2$ (Alfa). The mixture was fused at 200°C under vacuum for complete removal of residual methanol occluded in I and sealed under vacuum. The entire tube was heated at 280°C with stirring

for 1 hr. The workup procedure was identical to II and the yield was 59%. Analysis. Calc. for $C_{92}H_{72}N_8O_4Pt$: Pt, 12.60; C, 71.35; H, 4.69; N, 7.24. Found: Pt, 10.94; C, 73.31; H, 4.65; N, 7.75. IR (Supported film on NaCl) 3090-3030 ($=C-H$), 1608 ($C=C$), 1510-1470 (aromatic). Visible-UV (dioxane) 651 ($\epsilon=0.93 \times 10^5$ l/cm mole), 605, 394, 278.

Preparation of Monolayers of Cumylphenoxy Phthalocyanines

A Teflon coated pyrex trough 11 cm x 40 cm x 0.5 cm was used as the film balance tray for preparing monolayers of the metal free and metal substituted cumylphenoxy phthalocyanines and for determining their monolayer properties. Teflon coated glass rods 15 cm x 0.4 cm x 0.6 cm were used as barriers to compress the films adsorbed at the water surface and to sweep the water surface of adsorbed contaminants. A Wilhelmy plate was used to measure changes in the surface tension. The plate is of platinum, 2.0 cm x 1.5 cm x 0.005 cm. It is attached to a Statham UC 2 strain gauge and via an appropriate resistance bridge circuit to a strip chart recorder. The system can be calibrated to easily detect film pressures of 0.05 m N/m. The moveable Teflon barriers were coupled with a variable speed motor drive to permit continuous controlled compression of an adsorbed film. The rate of compression is maintained sufficiently slow so the resulting surface tension vs. film pressure curves are independent of compression rate. The film balance system is enclosed in a Lucite box to maintain a relatively dust-free environment during the course of a run. The measurements are carried out at room temperature, generally $25^0 \pm 2^0C$.

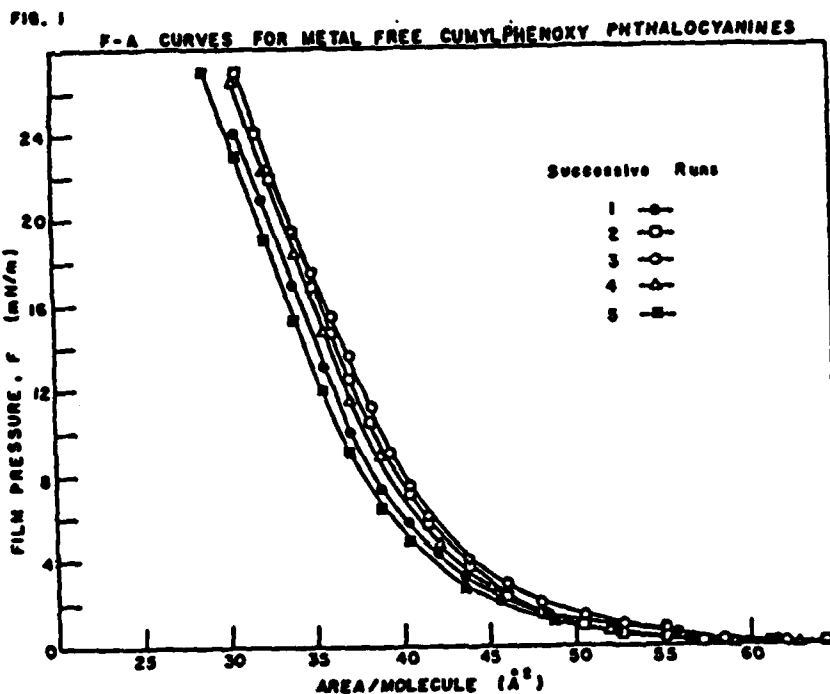
Solutions of metal free and metal containing (H_2 , Cu, Ni, Co, Pt, Pd) cumylphenoxy phthalocyanines were prepared in benzene. All glassware was acid cleaned, rinsed profusely with distilled water and dried prior to use. Solutions were delivered to the water surface from a micrometer syringe. In these initial studies the substrate used was 0.01 N HCl.

Prior to a run the film balance was washed with a detergent, rinsed with distilled water, drained and filled with substrate. The surface was cleaned by appropriate sweeping with the film barriers until no changes in film pressure were observed when the surface was swept to within 0.5 cm of the Wilhelmy plate mounted 2 cm from the end of the trough. The spreading solution was added dropwise to the surface and allowed to equilibrate while the solvent evaporated, usually 10 to 15 minutes. The Wilhelmy plate was cleaned by flaming to red heat, cooled and lowered until it just touched the surface and was wet by the substrate. The film was then compressed slowly and the film pressure vs. area/molecule curves recorded. The film balance is also equipped with a motor driven dip coater to transfer Langmuir-Blodgett films to solid surfaces by lowering and raising the substrate surfaces through the monolayer covered interfaces.

DISCUSSION

Monomolecular Films of Metal Free and Metal Substituted Cumylphenoxy Phthalocyanines

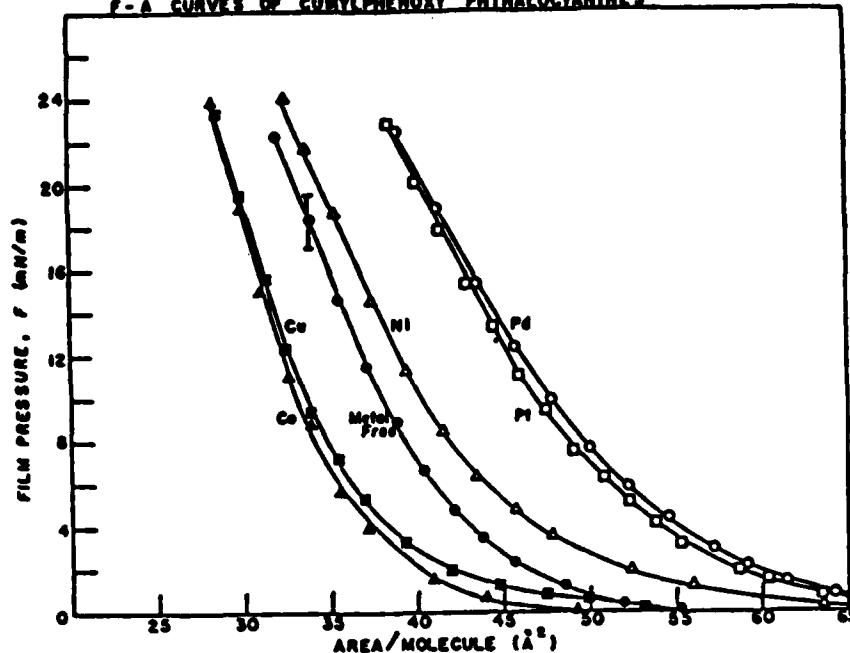
The cumylphenoxy phthalocyanines as anticipated formed stable, insoluble monomolecular films at the water/air interface. In figure 1 are given the Film Pressure vs. Area/Molecule (F-A) curves for 5 repetitive determinations for the metal free compound. All subsequent determinations



fell within the range of this data. The variation in the F-A curves is greater than that observed for most insoluble, stable film forming compounds, such as stearic acid. The cause of the unexpectedly large variation is the subject of a further investigation. It is likely related to the tendency of phthalocyanines to strongly associate, and the as yet unspecified effect of spreading solvent, solution concentration and surface forces on the associated complex. The monomolecular films are stable at film pressures up to film pressures of 20 mN/m, losing only a few tenths of a mN/m on being held at a given area/molecule for several minutes. The shape of the F-A curves are essentially independent of the rate of film compression up to film pressures of 10 to 15 mN/m. The variation in F-A curves for successive determinations is statistically the same for the metal containing derivatives as for the metal free. In figure 2, the F-A curves for the H_2 , Cu, Ni, Pt, Pd, and Co cumylphenoxy phthalocyanines are

FIG. 2

F-A CURVES OF CUMYLPHENOXY PHTHALOCYANINES



presented as the mean of 5 to 10 independent determinations. The standard deviation is given at 18 mN/m film pressure for the H₂ compound.

It is often assumed that a "significant" increase in film pressure is first detected when the adsorbed molecules are compressed by the film barriers until they are just in continuous contact, in whatever equilibrium orientation they assumed at larger areas/molecule in the absence of external force. This arbitrary "state" of the film occurs at film pressures less than 1 mN/m. This onset film pressure increases with compression, the shape of a F-A curve at low film pressures, and the area/molecule determined by extrapolation of the linear portion of a F-A curve (taken to liquid film pressure) to zero film pressures can each be used to help characterize the orientation and packing of adsorbed molecules. It is interesting to observe from the data in figure 2 that at low film pressures there must be significant differences in the orientations of the various phthalocyanine derivatives due to the presence of the specific metal atoms. For example the areas occupied per molecule vary at 1 mN/m from 42.5 Å² for the Co compound to 64.0 Å² for the Pd derivative. A second synthesis of Pt substituted cumylphenoxy phthalocyanine was done since spectral and elemental analysis indicated a trace of impurity. Monolayer data on this compound gave somewhat larger area/molecules at equivalent film pressures, in fact the average values were somewhat larger than those for the Pd derivative. It is also interesting that 64 Å² approaches the area that

would be occupied by the phthalocyanine nucleus lying in the plane of the interface with the phenoxy groups directed out of the interface and that 42.5 \AA^2 approximates the area that would be occupied if the planar phthalocyanine nucleus were oriented essentially perpendicular to the interface. It is planned to investigate other metal complexes and to compare the data with ball model measurements and with the degree of association as determined from vapor phase osmometry to better determine the molecular orientation.

Further compression of the adsorbed films to higher film pressures will initially force the individual molecules into closer contact, causing a molecular re-orientation to smaller apparent surface areas per molecule, and then to a collapse of the film with some molecules forced out of the interface. It is apparent that the effect of the various complexing metals, that were observed at low film pressures, persist at higher film pressures.

Electrical Measurements in Organic Films

Microelectrode arrays were fabricated on silica with interdigital gold electrodes 20 microns in width, spaced $7,000 \text{ \AA}$ apart. Due apparently to poor wettability of the gold electrodes by the cumylphenoxy phthalocyanine films uniform Langmuir-Blodgett films could not be transferred reproducibly to the electrode arrays. However, uniform L-B films could be prepared on clean glass. Electrodes of other metals will be fabricated for future electrical measurements.

Even though satisfactory Langmuir-Blodgett transfer films could not be prepared, thin films of metal free phthalocyanine could be sublimed onto a quartz/gold surface conductivity cell and I-V curves obtained in a helium atmosphere at room temperature under subdued light conditions. The curves were linear in the range of ± 2.5 volts and exhibited negligible hysteresis. The surface resistivity observed under these conditions was approximately 1.2×10^{15} ohms per square and was quite reproducible. The absence of charge injection by the electrodes (typified by nonlinearities in the I-V curve) and the apparent absence of polarization effects during measurements on this very weakly conducting organic semiconductor demonstrates the capabilities of the measurement scheme.

CONCLUSIONS

A series of cumylphenoxy phthalocyanines (H_2 , Co, Cu, Ni, Pt and Pd) has been synthesized and characterized. They were shown to have appreciable solubility in such solvents as benzene and toluene and to form stable monomolecular films at the water/air interface. The cumylphenoxy phthalocyanine derivatives were found to orient at the water/air interface with one edge of the planar ring directed towards the interface, with the planar ring itself oriented more or less perpendicular to the surface in a "slipped plane" arrangement. The degree of molecular packing was also discovered to be dependent on the identity of the complexed metal atoms in the ring. Considerable intermolecular association is indicated and may be influenced in some way by the film forming procedures used. The resulting

monolayers can be transferred as Langmuir-Blodgett films to clean substrates of quartz and silica, but do not transfer well to the gold used in the electrode arrays. Studies are now underway to determine the electrical properties of these phthalocyanine monolayers on new electrode arrays and to determine their sensitivity to toxic gases and simulants.

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